(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 708 184 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:
24.04.1996 Bulletin 1996/17

(21) Application number: 94914608.8

(22) Date of filing: 12.05.1994

(51) Int. Cl.^{6}: C22C 38/54

(86) International application number: PCT/JP94/00767

(87) International publication number:
WO 94/26947 (24.11.1994 Gazette 1994/26)

(84) Designated Contracting States:
DE DK FR GB NL SE

(30) Priority: 13.05.1993 JP 111957/93

(71) Applicant: NIPPON STEEL CORPORATION
Tokyo 100 (JP)

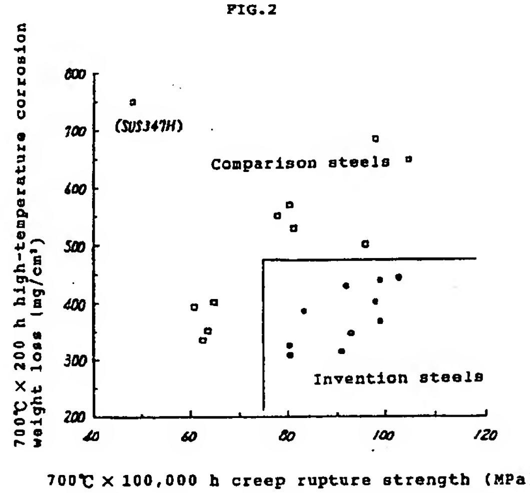
(72) Inventors:
- MIMURA, Hiroyuki,
  Nippon Steel Corp.
  Futtsu-shi, Chiba 299-12 (JP)
- KIKUCHI, Masao,
  Nippon Steel Corp.
  Futtsu-shi, Chiba 299-12 (JP)
- ARAKI, Satoshi,
  Nippon Steel Corp. Hikari Works
  Yamaguchi 743 (JP)
- NAOI, Hisashi,
  Nippon Steel Corp.
  Futtsu-shi, Chiba 299-12 (JP)

(74) Representative: Sandmair, Kurt, Dr. Dr.
Patentanwälte
Schwabe, Sandmair, Marx
Stuntzstrasse 16
D-81677 München (DE)

(54) HIGH-STRENGTH AUSTENITIC HEAT-RESISTING STEEL WITH EXCELLENT WELDABILITY AND GOOD HIGH-TEMPERATURE CORROSION RESISTANCE

(57) A high-strength austenitic heat-resisting steel that has excellent weldability and good high-temperature corrosion resistance and can exhibit excellent performance when used as the material of boilers to be used under the conditions becoming more and more severe. The steel comprises less than 0.02 % (by mass, the same will apply hereinbelow) of carbon, at most 1.5 % of silicon, 0.3-1.5 % of manganese, at most 0.02 % of phosphorus, at most 0.005 % of sulfur, 18-26 % of chromium, 20-40 % of nickel, 0.5-10.0 % of tungsten, 0.05-0.4 % of niobium, 0.01-0.2 % of titanium, 0.003-0.008 % of boron, 0.05-0.3 % of nitrogen, and if necessary at least one member of 0.5-2.0 % of molybdenum and/or 0.001-0.05 % of magnesium, 0.001-0.05 % of calcium and 0.001-0.15 % of rare earth element (REM), and the balance consisting of iron and inevitable impurities.

FIG.2



EP 0 708 184 A1

Description

Technical Field

This invention relates to an austenitic heat-resistant steel exhibiting outstanding high-temperature strength, excellent weldability and good high-temperature corrosion resistance property and displaying excellent performance when utilized in boilers, which are experiencing increasingly harsh use environments.

Background Art

From the points of improved economy and the recent move to suppress carbon dioxide gas emissions, thermal power plants are planning extra super critical temperature boilers with high-temperature, high-pressure steam conditions. As pointed out in "Iron and Steel" No.70, p.S-1409 and "Thermal and Nuclear Power Generation" vol.38, p.75, high-strength steels developed for withstanding use in such harsh environments include austenitic heat-resistant steels utilizing precipitation strengthening by carbo-nitrides of Nb, Ti and the like and solution strengthening by Mo.

Since these heat-resistant steels contain large amounts of alloying elements, however, they cannot be considered easy to weld in comparison with conventional austenitic heat-resistant steel such as SUS347H and, as such, have a problem regarding welding workability.

Increasing steel purity, specifically, reducing P and S content together with reduction of C content, is know as an effective means of improving weldability. Since as just mentioned, however, most heat-resistant steels are strengthened by carbo-nitrides, reduction of C content leads to reduction of high-temperature strength.

On the other hand, it is known that increasing the content of Mo frequently added for the purpose of solution-strengthening a steel degrades high-temperature corrosion resistance property.

The object of this invention is to provide an austenitic heat-resistant steel that exhibits good weldability and is excellent in high-temperature strength and high-temperature corrosion resistance property.

Disclosure of the Invention

The inventors conducted various experiments regarding steel added with Mo and W in order to offset by solution strengthening the loss of high-temperature strength caused by reduction of C content and, as a result, succeeded in developing a heat-resistant steel which maintains high-temperature strength at a low C content while also securing high-temperature corrosion resistance property. Specifically, the gist of this invention is as follows:

(1) A high-strength austenitic heat-resistant steel excellent in weldability and good in high-temperature corrosion resistance property characterized in that it comprises, in mass percent,

C :	less than 0.02%,
Si :	not more than 1.5%,
Mn :	0.3 - 1.5%,
P :	not more than 0.02%,
S :	not more than 0.005%,
Cr :	18 - 26%,
Ni :	20 - 40%,
W :	0.5 - 10.0%,
Nb :	0.05 - 0.4%,
Ti :	0.01 - 0.2%,
B :	0.003 - 0.008%, and
N :	0.05 - 0.3%,

the balance being Fe and unavoidable impurities.

(2) A high-strength austenitic heat-resistant steel excellent in weldability and good in high-temperature corrosion resistance property according to paragraph (1) above further containing

Mo : 0.5 - 2.0%.

(3) A high-strength austenitic heat-resistant steel excellent in weldability and good in high-temperature corrosion resistance property according to paragraph (1) or (2) above further containing one or more of

Mg : 0.001 - 0.05%,

Ca :	0.001 - 0.05%, and
Rare earth elements (REM) :	0.001 - 0.15%.

Brief Description of Drawings

Figure 1 is a graph showing the effect of Mo and W on the high-temperature corrosion resistance property of 20 Cr - 25 Ni steel.

Figure 2 is a graph comparing the creep rupture strengths and high-temperature corrosion weight losses of invention steels and comparison steels.

Figure 3 is a graph showing the results of Varestraint tests conducted on steels containing the main alloying elements other than C within the ranges of the invention and on SUS347H.

Best Mode for Carrying out the Invention

The reasons for setting the ranges of the alloying elements in the invention in the foregoing manner will be explained.

C :

It is necessary to reduce C content as far as possible for preventing high-temperature cracking during welding and ductility degradation. Based on tests, the upper limit of C content was set as follows for securing good weldability. Figure 3 shows the results of an evaluation of weldability by Varestraint tests conducted on steels containing the main alloying elements other than C within the ranges of the invention (Cr : 20%, Ni : 25%, W : 3%) and having varied C content (■ in the drawing) and on SUS347H (corresponding to comparison steel K in the examples set out later; □ in the drawing). The conditions of the test were, test piece thickness : 5 mm, welding method : GTAW, welding voltage : 10 V, welding current : 80 A, welding velocity : 80 mm/min, and applied strain : 2%. Based on the tests results, and aiming at a content on a par with SUS347H, the upper limit of C content for securing good weldability is set at less than 0.02%.

Si :

Si not only is effective as a deoxidizing agent but is also an element which improves oxidation resistance and high-temperature corrosion resistance property, but an excessive Si content reduces creep rupture strength, toughness and weldability. The upper limit is therefore set at 1.5%.

Mn :

Mn is an element which has deoxidizing activity and improves weldability and hot workability. For obtaining sufficient deoxidation and a sound ingot, the lower limit of Mn is set at 0.3%. Since an excessive Mn content degrades oxidation resistance, however, the upper limit is set to 1.5%.

Cr :

Cr is an indispensable element for oxidation resistance, water vapor oxidation resistance and high-temperature corrosion resistance property. For securing properties at least as good as prior art austenitic stainless steels, the lower limit of Cr content is set at 18%, which is the same as the Cr content of austenitic stainless steels. However, since increasing Cr content lowers the stability of the austenite and weakens the high-temperature strength and further promotes formation of an intermetallic compound σ phase and reduces toughness, the upper limit is set at 26%.

Ni :

Ni is an element required for increasing the stability of the austenite and suppressing formation of an intermetallic compound σ phase. An Ni content of not less than 20% is necessary for ensuring stability of the austenite against the content of Cr and other ferrite forming elements. On the other hand, since an Ni content exceeding 40% is disadvantageous from the aspect of price, the Ni content is set at 20 - 40%.

Mo, W :

Mo and W are both elements which markedly increase high-temperature strength as by entering solid solution. Neither has much effect when added at less than 0.5%, while addition of W at more than 10% leads to precipitation of intermetallic compounds such as Laves phase and reduces creep rupture ductility. When Mo is added alone, the high-

temperature corrosion resistance property worsens as the Mo content increases. On the other hand, tests show that adding W alone does not degrade the high-temperature corrosion resistance property and that adding it in combination with Mo improves the high-temperature corrosion resistance property over that of a steel added with Mo alone. Therefore, W is always added, and the range thereof is set at 0.5 - 10%. As Mo in particular degrades the high-temperature corrosion resistance property when added in excess of 2.0%, even when added in combination with W, it is added, when required, at 0.5 - 2.0%.

Nb, Ti :

Nb and Ti markedly improve long-term creep rupture strength by forming minute carbo-nitrides. Since this effect is not obtained when the Nb content is less than 0.05% or the Ti content is less than 0.01%, the lower limits of Nb and Ti content are set at 0.05% and 0.01%. Although the aforesaid effect becomes more pronounced as the content of Nb and Ti soluble at the solid solution treatment temperature increases, adding Nb and Ti in excess of the solution limit degrades the creep rupture strength owing to the undissolved carbo-nitrides that remain. Therefore, the upper limits of Nb and Ti content are set at 0.4% and 0.2%, and for increasing the solid solution (Nb + Ti) content within these ranges, Nb and Ti are added in combination.

B :

B is an element which has the effect of enhancing intergranular strength and increasing creep rupture strength. However, since this effect is small at less than 0.003% and a content exceeding 0.008% degrades weldability and hot workability, the B content range is set at 0.003 - 0.008%.

P :

Since P markedly degrades weldability when added in a large amount, its upper limit is set at 0.02%.

S :

Since S segregates at the grain boundaries and degrades hot workability and also promotes intergranular brittleness during creep, its upper limit is set at 0.005%.

N :

N is an element which markedly improves creep rupture strength by solution strengthening and formation of nitrides. At a content of less than 0.05%, N cannot offset the loss of strength resulting from the reduction of C content for improving weldability, while addition at more than 0.3% produces little increase in long-term creep rupture strength but degrades toughness. Therefore, the N content range is set at 0.05 - 0.3%.

Mg, Ca, rare earth elements (REM)

While these elements purify the steel by deoxidation and desulfurization, thereby enhancing hot workability, for obtaining this effect it is necessary to add at least one of them at not less than 0.001%. However, since addition in excess of Mg : 0.05%, Ca : 0.05%, REM : 0.15% has the opposite effect of impairing hot workability, the respective addition ranges are set at Mg : 0.001 - 0.05%, Ca : 0.001 - 0.05%, REM : 0.001 - 0.15%.

Examples

The invention will now be explained with reference to specific examples.

Table 1 and Table 2 (continued from Table 1) show the chemical compositions and material properties of tested steel specimens. After solution treatment at 1250°C , these steels were subjected to creep rupture test at 700 and 750°C and to high-temperature corrosion test at 700°C . The creep rupture strength data was organized using the Larson-Miller method for estimating the 700°C x 100,000 h rupture strength. The high-temperature corrosion test was conducted by immersing the steel specimen in simulated coal-fired boiler ash of K_2SO_4 : Na_2SO_4 : $Fe_2(SO_4)_3$ = 0.28 : 0.2 : 0.5 (mass ratio) for 200 h and then measuring the corrosion weight loss. The test results are shown in Table 2.

Among the steels shown in Tables 1 and 2, A - J are invention steels and K - U are comparison steels. Among the comparison steels, K corresponds to the widely used SUS347H. The invention steels have high-temperature strengths and high-temperature corrosion resistance properties that are very superior in comparison with the SUS347H steel. Among the comparison steels, L - O are examples having low high-temperature strength because they contain neither

Mo or W and their Nb or B content is outside the range of the invention. P - U are examples with relatively high high-temperature strength but having poor high-temperature corrosion resistance property notwithstanding addition of Mo alone or in combination with W, owing to large Mo content.

Figure 1 shows the effect of Mo and W on the high-temperature corrosion resistance property of 20 Cr - 25 Ni steel. While corrosion weight loss is large when Mo is added alone (● in the drawing), it will be noted that the high-temperature corrosion resistance property is improved when W is added in combination at 1.5% (▲ in the figure). It can further be seen that the corrosion weight loss does not change when W is added alone (□ in the figure).

Figure 2 compares the creep rupture strengths and high-temperature corrosion weight losses of invention steels and comparison steels. It can be seen that the comparison steels are inferior in one or both of the high-temperature strength and the high-temperature corrosion resistance property, while the invention steels excel in both high-tempera-

ture strength and high-temperature corrosion resistance property.

Table 1

		Chemical composition (mass %)										
		C	Si	Mn	P	S	Cr	Ni	Mo	W	Nb	Ti
INVENTION STEELS	A	0.014	0.49	1.05	<0.002	<0.001	20.0	24.0	–	1.53	0.20	0.09
	B	0.015	0.49	1.06	<0.002	<0.001	20.7	24.8	–	3.24	0.21	0.11
	C	0.016	0.50	1.01	<0.002	0.002	19.8	23.9	1.37	1.50	0.20	0.08
	D	0.018	0.50	1.08	<0.002	<0.001	20.9	24.8	1.54	3.34	0.21	0.12
	E	0.016	0.47	1.01	<0.002	<0.001	20.2	24.0	–	4.91	0.23	0.10
	F	0.013	0.48	0.90	<0.002	<0.001	20.1	24.5	1.56	4.64	0.21	0.09
	G	0.015	0.48	1.06	<0.002	0.002	20.2	25.0	–	8.12	0.18	0.08
	H	0.017	0.49	1.03	<0.002	0.002	24.3	34.6	–	1.50	0.23	0.07
	I	0.011	0.48	0.99	<0.002	<0.001	24.4	34.6	1.46	1.47	0.23	0.07
	J	0.016	0.47	1.00	<0.002	<0.001	25.0	34.4	1.50	3.18	0.23	0.08
COMPARISON STEELS	K	0.050*	0.49	1.36	0.014	0.005	18.3	11.3*	–*	–*	0.98*	–*
	L	0.019	0.98	0.87	0.025*	0.005	20.6	24.7	–*	–*	0.42*	0.07
	M	0.019	0.46	1.06	<0.002	<0.001	20.0	24.7	–*	–*	–*	0.17
	N	0.016	0.52	1.01	0.005	0.003	19.6	24.3	–*	–*	0.17	0.06
	O	0.015	0.47	1.00	0.004	<0.001	19.9	25.0	–*	–*	0.21	0.10
	P	0.019	0.53	1.01	<0.002	<0.001	20.3	25.1	1.44	–*	0.21	0.09
	Q	0.016	0.49	0.99	<0.002	0.002	20.4	25.2	2.79*	–*	0.20	0.10
	R	0.015	0.48	1.00	<0.002	0.002	20.0	24.0	2.81*	1.49	0.20	0.08
	S	0.017	0.46	1.07	0.002	0.002	20.0	24.4	4.38*	–*	0.20	0.12
	T	0.021*	0.52	1.04	<0.002	0.002	20.2	24.8	4.03*	4.56	0.23	0.10
	U	0.019	0.46	0.93	<0.002	0.002	24.2	34.2	4.02*	–*	0.21	0.06

*This mark indicates that the content is outside the composition range of this invention

Table 2 (continued from Table 1)

		Chemical composition (mass %)					700℃×100,000h creep rupture strength (MPa)	700℃×200h corrosion weight loss (mg/cm²)
		B	N	Mg	Ca	REM		
INVENTION STEELS	A	0.0052	0.133	–	–	–	83	386
	B	0.0043	0.147	–	–	–	93	346
	C	0.0058	0.125	–	0.0074	–	92	429
	D	0.0041	0.147	–	0.0056	–	99	439
	E	0.0045	0.137	–	–	–	98	402
	F	0.0053	0.098	–	0.0045	–	103	444
	G	0.0035	0.140	–	–	–	99	366
	H	0.0051	0.098	0.0035	0.0048	–	80	307
	I	0.0049	0.139	–	–	0.006Ce	80	324
	J	0.0045	0.141	–	–	0.012Ce	91	313
COMPARISON STEELS	K	–*	0.008*	–	–	–	48	750
	L	0.0051	0.155	–	–	–	61	394
	M	0.0051	0.042	–	–	–	65	402
	N	–*	0.170	–	–	–	63	335
	O	0.0042	0.095	–	0.0065	–	64	350
	P	0.0041	0.099	–	0.0051	–	78	551
	Q	0.0044	0.100	–	0.0032	–	80	569
	R	0.0055	0.122	–	0.0040	–	96	502
	S	0.0047	0.097	–	–	–	98	685
	T	0.0051	0.124	–	0.0020	–	105	648
	U	0.0052	0.094	–	–	–	81	528

*This mark indicates that the content is outside the composition range of this invention

Industrial Applicability

This invention enables realization of an austenitic heat-resistant steel that is excellent in weldability and secures high-temperature strength and high-temperature corrosion resistance property. It facilitates application of high-strength steel to high-temperature, high-pressure boilers and enables a reduction of implementation cost.

Claims

1. A high-strength austenitic heat-resistant steel excellent in weldability and good in high-temperature corrosion resistance property characterized in that it comprises, in mass percent,

C :	less than 0.02%,
Si :	not more than 1.5%,
Mn :	0.3 - 1.5%,
P :	not more than 0.02%,
S :	not more than 0.005%,
Cr :	18 - 26%,
Ni :	20 - 40%,
W :	0.5 - 10.0%,
Nb :	0.05 - 0.4%,
Ti :	0.01 - 0.2%,
B :	0.003 - 0.008%, and
N :	0.05 - 0.3%,

the balance being Fe and unavoidable impurities.

2. A high-strength austenitic heat-resistant steel excellent in weldability and good in high-temperature corrosion resistance property according to claim 1 further containing

Mo : 0.5 - 2.0%.

3. A high-strength austenitic heat-resistant steel excellent in weldability and good in high-temperature corrosion resistance property according to claim 1 or 2 further containing one or more of

Mg :	0.001 - 0.05%,
Ca :	0.001 - 0.05%, and
Rare earth elements (REM) :	0.001 - 0.15%.

FIG.1

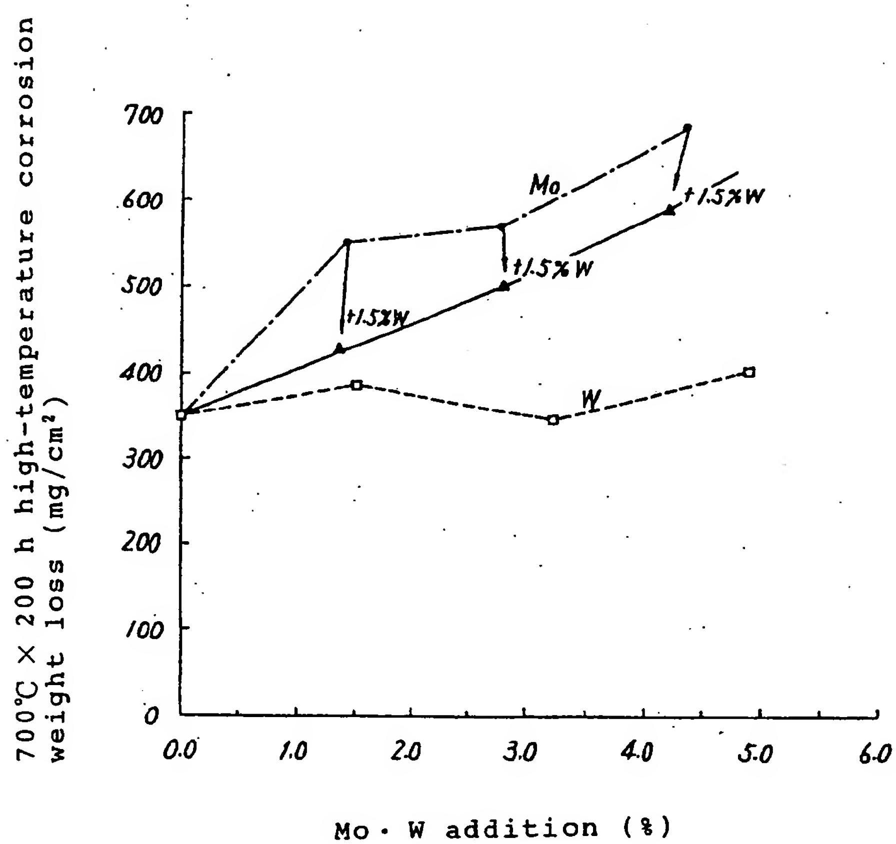

700°C × 200 h high-temperature corrosion weight loss (mg/cm²)
700
600
500
400
300
200
100
0
Mo
+1.5%W
+1.5%W
+1.5%W
W
0.0
1.0
2.0
3.0
4.0
5.0
6.0
Mo · W addition (%)

FIG.2

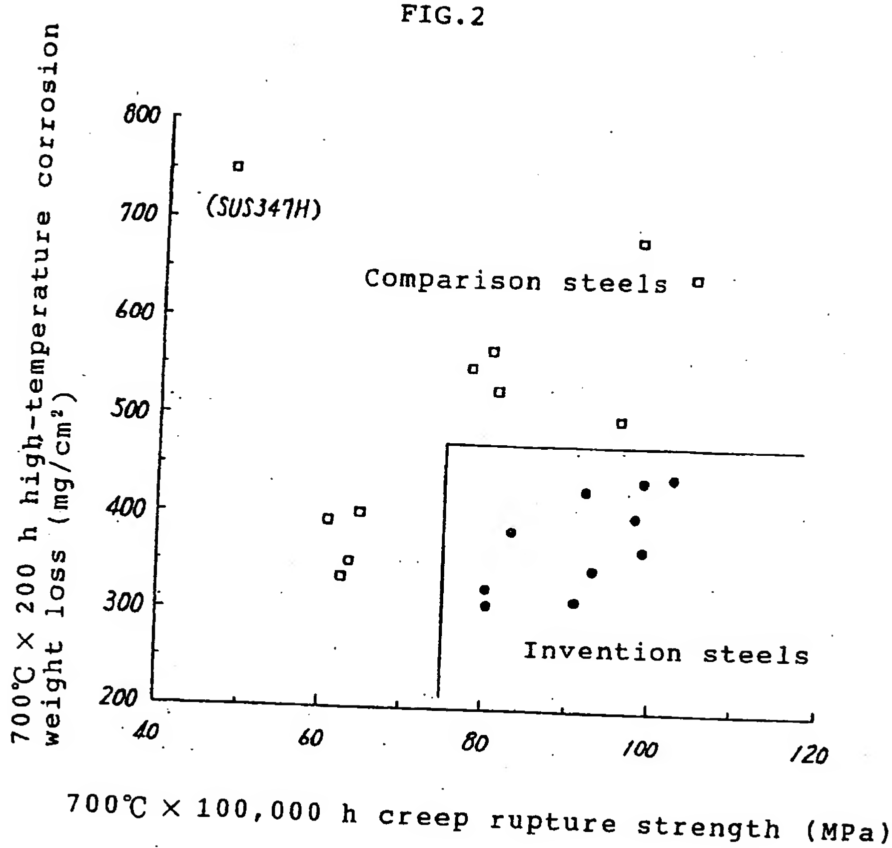
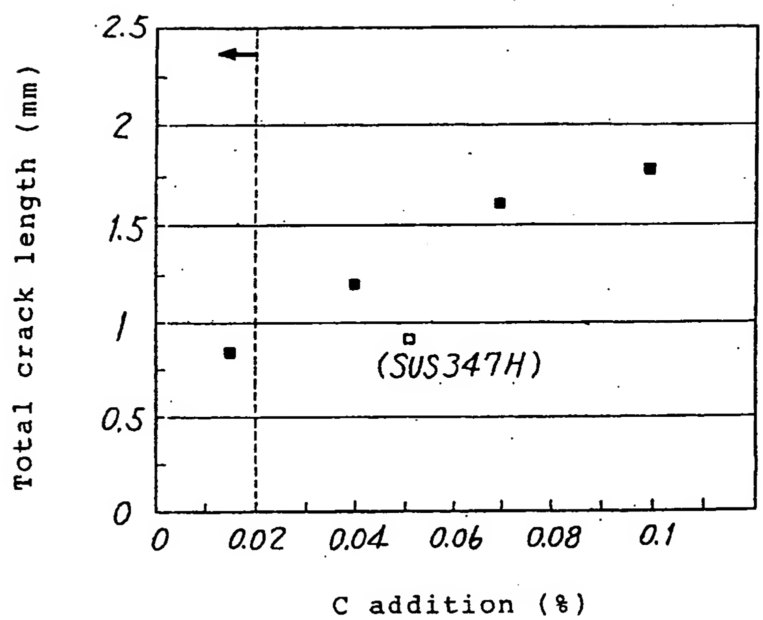

700℃ × 200 h high-temperature corrosion weight loss (mg/cm²)
800
700
600
500
400
300
200
(SUS347H)
Comparison steels
Invention steels
40
60
80
100
120
700℃ × 100,000 h creep rupture strength (MPa)

FIG.3


Total crack length (mm)
2.5
2
1.5
1
0.5
0
(SUS347H)
0
0.02
0.04
0.06
0.08
0.1
C addition (%)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP94/00767

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl^5 C22C38/54

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl^5 C22C38/00-38/60

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A, 63-183155 (Nippon Steel Corp.), July 28, 1988 (28. 07. 88), Lower left column, page 1, (Family: none)	1, 2
A	JP, B2, 63-44814 (Daido Steel Co., Ltd.), September 7, 1988 (07. 09. 88), Lines 16 to 23, column 1, lines 3 to 11, column 6, (Family: none)	3
A	JP, B2, 62-54179 (Daido Steel Co., Ltd.), November 13, 1987 (13. 11. 87), Lines 9 to 17, column 1, lines 2 to 11, column 2, lines 11 to 21, column 6, (Family: none)	3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
July 26, 1994 (26. 07. 94)	August 9, 1994 (09. 08. 94)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)